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**CONTROL OF NATURAL GAS HYDRATES**

Measurement and Modeling of the Rate of Decomposition of a Hydrate Plug

**Final Report**

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## 1.0 Executive Summary

In this work we examined hydrate plug decomposition by depressurization (venting) and chemical injection. We also developed a mathematical model for the plug depressurization process. The model was validated experimentally by measuring the rate of decomposition of hydrate plugs in a 2 inch internal diameter, 38.5 inch long pipe. A detailed description of the testing device and the experimental procedure is given in this report.

The results showed that hydrate blockage removal using depressurization is a slow process when conducted at low temperature and small pressure reduction. We also concluded that the hydrate plug decomposition process follows different modes depending on the ambient temperature and the magnitude of the pressure reduction.

The results also indicated that hydrate plug decomposition by chemical injection can be an effective process for blockage removal when depressurization is not possible. Ethylene glycol proved to be a more effective chemical than methanol or salt solution.

## 2.0 Introduction

Four basic schemes have been suggested to remove a hydrate blockage from subsea gas or gas condensate pipelines. These schemes are: (1) depressurization, (2) thermal, (3) chemical and (4) mechanical. In the first scheme, depressurization, the pipeline pressure is reduced below the hydrate equilibrium pressure at the seabed temperature. Consequently, the hydrate blockage starts to dissociate at the boundary subjected to the pressure reduction. The heat of dissociation will be absorbed from the vicinity of the melting front creating a temperature gradient with the surrounding environment. The heat flows under this temperature gradient from the surrounding environment to the hydrate plug which will continue to dissociate unless the pipeline pressure is allowed to build up to a new equilibrium value that corresponds to the lower temperature. In the thermal scheme an external source of energy is utilized to raise the pipeline temperature above the hydrate equilibrium temperature. Heat tracing and hot fluids circulation are some of the possible means. The third scheme involves bringing inhibitors like methanol or glycol into direct contact with the hydrate blockage to shift the phase equilibrium line and destabilize the hydrate. In the fourth scheme, the hydrate blockage is removed by boosting the pipeline pressure, pigging or drilling.

Under current pipeline design and operating conditions, depressurization and chemical injection are the most viable options to remove hydrate blockages from subsea natural gas or gas

condensate pipelines. In this work, we examined these two options under various operating conditions and developed and verified a mathematical model for the depressurization scheme.

### 3.0 Experimental Set-up and Procedure

The hydrate plug formation and decomposition tests were carried out using the device shown in **Fig. 1**. The device was designed and assembled as the first part of the project. The device consists of two concentric pipes. The inner pipe is made of 316 stainless steel and rated to 2000 psia. The pipe has a length of 38.5 inch, an internal diameter of 2 inch, and a wall thickness 0.5 inch. The hydrate formation and decomposition is detected by 16 pairs of infrared light transmitters and receivers diametrically positioned across the inner pipe. A magnetic mixer is attached to the bottom end of the pipe to enhance the rate of hydrate formation. The external pipe is an 8 inch diameter PVC tube which is used as a cooling jacket. A Lauda RMS circulating cooler is used to control the jacket temperature by circulating water. A high pressure gas supply cylinder is used to pressurize the pipe with the gas, a mixture of 96% methane and 4% propane. A back pressure regulator is used to maintain constant back pressure (venting pressure) on the hydrate plug during the decomposition process. The vented gas during the decomposition is measured using a DBR JEFRI gasometer with capacity of 0.040 m<sup>3</sup> and a resolution of 0.4E-6 m<sup>3</sup>. The pressure in the gas supply cylinder is measured with a Precise Sensors pressure transducer with a range of 0-7500 psia and an accuracy of  $\pm 0.075\%$  of span. The pipe pressure is measured with a Heise digital pressure indicator with a range of 0-2000 psia and an accuracy of  $\pm 0.07\%$  of span. The temperatures of the pipe and the gas supply cylinder are measured with Omega thermistors model ON-950 calibrated to 0.05°F. All the pressures and temperatures and the response from the light sensors and the gasometer are recorded using a data acquisition system.

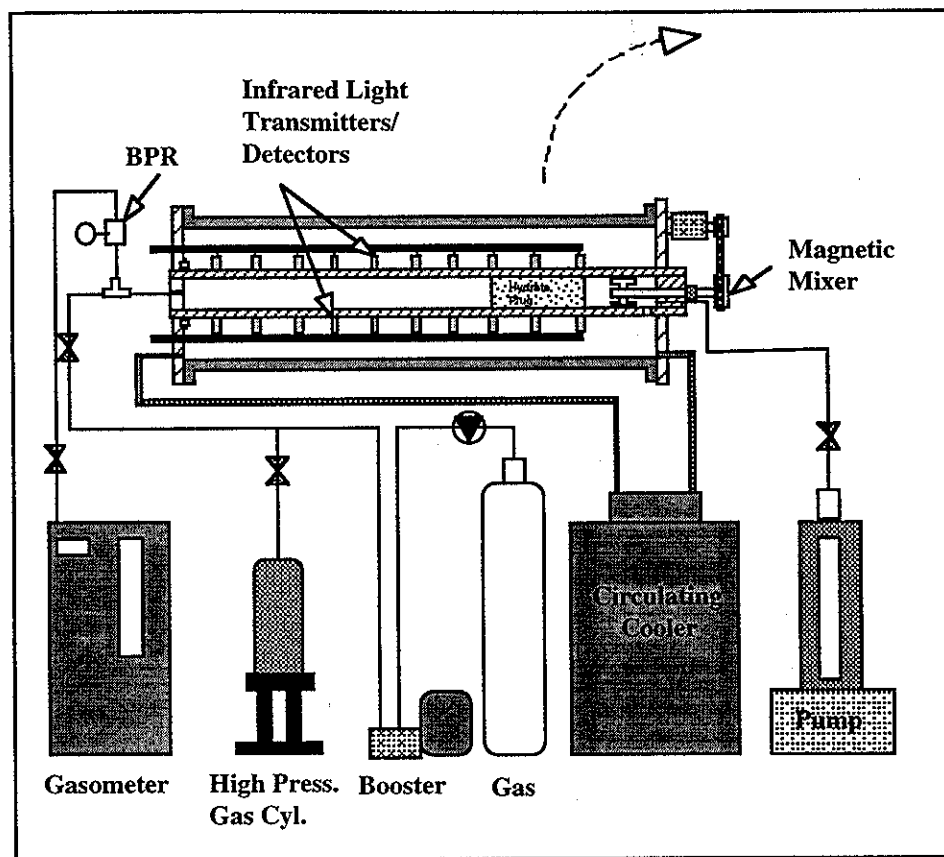


Figure 1- Hydrate Plug Decomposition Apparatus.

### 3.1 Hydrate Plug Formation

Initially, the pipe is set in a vertical position and charged with 600 ml of de-ionized water. A vacuum is applied to remove air from the pipe. The gas mixture is then introduced into the pipe from the gas supply cylinder until a pressure of 1000-1200 psia is obtained. The pipe temperature is lowered to 36°F using the circulating cooler. Under these conditions hydrates easily form while mixing. As the pressure in the pipe declines due to hydrate formation, more gas is introduced through the bottom end of the pipe from the gas supply cylinder. This way more hydrate is formed as the gas bubbles through the hydrate water mixture as it is stirred with the mixer. During this stage, hydrates form in such amounts that they stop (freeze) the mixer. To enhance hydrate growth even further an annealing process was used where the hydrate mass (plug) is subjected to several cycles of heating and cooling. This process enhances the conversion of water and gas to hydrates.

### 3.2 Hydrate Plug Depressurization

Normally the hydrate plug is aged 3 to 5 days before starting a depressurization run. The pressure in the dome of the back pressure regulator is set to the desired decomposition pressure. Then the pipe pressure is quickly reduced to the set back pressure by venting gas. The pipe is then turned horizontal and the gas from the hydrate decomposition is routed to the gasometer. From that point on, the run proceeds uninterrupted for 5 hours or when the plug is fully decomposed. The pressures, temperatures of the pipe and the gas supply cylinder, the gasometer reading, and the light sensors reading are all recorded at 20 second intervals.

### 3.3 Chemical Injection

All the chemical injection runs were performed with the pipe in vertical position. The tests were done using methanol, ethylene glycol, and NaCl solutions. After setting the pipe pressure to the desired value, the chemical is injected through the top end of the pipe in increments of 20-45 ml using high pressure syringe pump. As the hydrate starts to melt, the resulting gas is routed to the gasometer to measure its volume. An additional increment of chemical is injected each time the gas volume levels off.

## 4.0 Hydrate Plug Decomposition Model

Hydrate plug decomposition in a subsea pipeline can proceed in one or more of four different modes depending on the conditions under which the hydrate plug has formed. The four decomposition modes are:

1. Frontal decomposition (A plug that fills the entire cross-sectional area of the pipe with little or no pressure communication across it)
2. Linear decomposition (A fractured plug with the decomposition proceeding across the faces of the fractures)
3. Radial-Frontal (A plug that is loosely attached to the pipe walls)
4. Radial-Linear (A plug that is fractured and loosely attached to the pipe wall)

A single mathematical model incorporating all of the above decomposition modes, which is a two dimensional moving boundary problem, is a formidable task to undertake. Our objective was to use available analytical solutions to help estimate the effect of each of the above decomposition modes. Accordingly, we considered only one dimensional, semi infinite solutions for the linear and radial decomposition modes. In developing the mathematical model we assumed that the pipeline is not insulated and that the hydrate blockage is at equilibrium pressure

at seabed ambient temperature. The decomposition of the hydrate starts after reducing the pressure at the hydrate/gas interface below the hydrate equilibrium pressure at the seabed temperature. It is assumed that the gas and water produced from the decomposition process are instantaneously removed from the hydrate/gas interface. Since the thermal conductivity of the pipe is over 100 times that of the hydrate, we assumed that temperature at the internal walls of the pipe is equal to the seabed ambient temperature.

#### 4.1 Linear and Frontal Decomposition Modes

A schematic representation of a fractured hydrate plug decomposing in a linear mode is shown in Fig. 2. The temperature distribution within the plug can be described with the following Equation:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2} \quad (1)$$

$$\text{where } \alpha = \frac{k}{\rho c}$$

The initial conditions are:

$$\begin{aligned} Z(t) &= 0 & \text{at } t &= 0 \\ T(z, t) &= T_e & \text{at } t &= 0 \text{ and } 0 < z < \infty \end{aligned} \quad (2)$$

The boundary conditions at the moving boundary,  $z = Z(t)$  are:

$$\rho \Delta H_d \frac{dZ}{dt} = k \frac{\partial T}{\partial z} \quad (3a)$$

and

$$T = T_v \quad (3b)$$

Here  $T_v$  is determined from the following equation:

$$p_v = a \exp(bT) \quad (4)$$

where:  $a$  and  $b$  are constants for a particular gas composition.

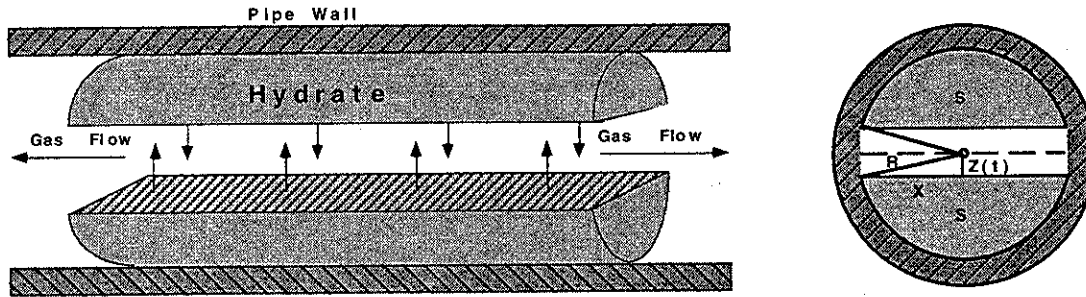


Figure 2

Equations 1 to 4 can be solved for the location of the moving boundary,  $Z(t)$  and the temperature profile,  $T(z,t)$ . An analytical solution is given in equations 5 and 6.

$$Z(t) = 2\lambda\sqrt{\alpha t} \quad (5)$$

$$T(z,t) = T_e - \sqrt{\pi} \frac{\Delta H_d}{c} \lambda e^{\lambda^2} \Phi^* \left( \frac{z}{2\sqrt{\alpha t}} \right) \quad (6)$$

## 4.2 Radial Decomposition Mode

A schematic representation of a hydrate plug decomposing in a radial mode is shown in **Fig. 3**. For the radial decomposition mode, the temperature distribution within the plug can be described with the following Equation:

$$\frac{\partial T}{\partial t} = \alpha \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) \quad (7)$$

$$\text{where } \alpha = \frac{k}{\rho c}$$

Initial conditions:

$$\text{At } t = 0, \quad 0 \leq r \leq R_0$$

$$T = T_e. \quad (8)$$

The boundary conditions at the moving boundary,  $r=R(t)$  are:

$$\rho \Delta H_d \frac{dR}{dt} = k \frac{\partial T}{\partial R} \quad (9a)$$

$$T = T_v \quad (9b)$$

Here  $T_v$  is determined from the following equation:

$$p_v = a \exp(bT) \quad (10)$$

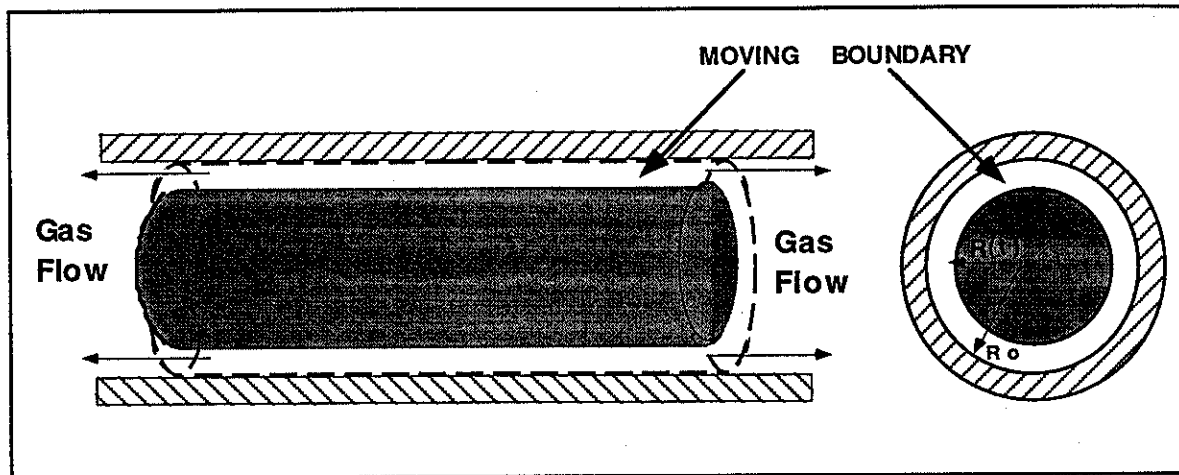


Figure 3

Equations 7 to 10 can be solved for the location of the moving boundary,  $R(t)$  and the temperature profile,  $T(r,t)$ . An analytical solution is given in equations 11 and 12.

$$R(t) = R_0 - 2\lambda_r \sqrt{\alpha t} \quad (11)$$

$$T(r,t) = T_e + (T_v - T_e) \frac{Ei\left(-\frac{r^2}{4\alpha t}\right)}{Ei(-\lambda_r^2 t)} \quad (12)$$

### 4.3 Results and Model Verification

A total of twenty five successful hydrate plug decomposition runs were conducted. These runs are listed in **Table 1**. Given the nature of the hydrate formation process, it is almost impossible to form two identical plugs. In order to form hydrate plugs that are relatively homogeneous and consistent an annealing process was used, where the plug is subjected to several cycles of heating and cooling. This process enhances the conversion of water and gas to hydrates. For model verification, we used the five hydrate plug decomposition runs listed in **Table 2**. Non-sealing plugs formed in all of these runs with full pressure communication across the plugs. Consequently, the plugs were treated as a fractured mass of hydrates. The decomposition process for all plugs, except run R23D were assumed to be taking place in a linear mode. A single fracture along the plug (**Fig. 2**) gave the best match to the model performance.



The volume of gas per unit length of the plug generated from hydrate decomposition is determined using Equations 13a and 13b.

$$V = GL(\pi R_o^2 - 2S) \quad (13a)$$

Where

$$S = R_o^2 \arctan \frac{\sqrt{R_o^2 - Z(t)^2}}{Z(t)} - Z(t) \sqrt{R_o^2 - Z(t)^2} \quad (13b)$$

Fig. 4 shows the gas production due to the plug decomposition for runs R15D, R16D, R17D, R20D and R23D. It is clear from Fig. 4 that the higher the pressure reduction,  $\Delta p$ , the faster the decomposition process is as indicated by the produced gas volume. For a given temperature,  $\Delta p$  is defined as the difference between the equilibrium pressure and the experimental pressure. The first three runs, R15D, R16D, and R17D, which were conducted at similar pressure and temperature conditions, resulted in similar gas production. On the other hand, run R20D, which was conducted at higher temperature and pressure reduction (50.48°F and 160.1 psia), resulted in much higher gas production. In run R23D, the pressure reduction was increased to 240.5 psia at 51.3°F. The produced gas volume of this run increased almost an order of magnitude over that of run R20D. We concluded that the increase in the produced gas volume is due to the change in the decomposition mode from linear to radial. The produced gas volume for run R23D is calculated using Equation 14.

$$V = GL(\pi R_o^2 - R(t)^2) \quad (14)$$

Although we have not observed this behavior in our study, subjecting the pipeline to large pressure reductions to melt hydrate blockages when the ambient temperature is close to 32°F could result in freezing the water coming from the decomposing hydrates.

Table 1- Summary of hydrate plug decomposition runs.

Run ID	P, psia	T, °F	Test Fluid	Notes
R2D.DAT	150	39.4	820 ml De-ionized water	Water reached sensor 5 (12" from bottom)
R3D	210	45.5	Same Water Sample	Gasometer was replaced
R4D	210	44.7	600 ml De-ionized water	Hydrate was still present when run was terminated (mixer jammed)
R5D	238	45	Same Water Sample	
R6D	131.9	38.3	Same Water Sample	Run was terminated when the HD ran out of storage space
R7D	184	51.15	Same Water Sample	
R8D	213	45.38	Same Water Sample	Hydrate was still present when run was terminated (mixer jammed)
R9D	212	45.24	Same Water Sample	Hydrate was still present when run was terminated (mixer jammed)
R10D	212	45.3	Same Water Sample	
R11D	213	45.3	Same Water Sample	
R12D	213	45.26	Same Water Sample	
R13D	210	45.25	Same Water Sample	Hydrate was still present when run was terminated (mixer jammed)
R14D	211	45.12	Same Water Sample	Run was aborted
R15D	210	45.25	Same Water Sample	
R16D	211	45.32	Same Water Sample	
R17D	211	45.4	Same Water Sample	
R18D	211	40.9	Same Water Sample	
R19D	211	50.26	Same Water Sample	
R20D	211	50.48	Same Water Sample	
R21D	211	49.52	Same Water Sample	No decomposition took place?
R22D	150	46.3	Same Water Sample	
R23D	150	51.42	Same Water Sample	587 ml of water was recovered after this run
R24D	108	40.22	600 ml De-ionized water	
R25D	110	41	Same Water Sample	
R26D	160	45.23	Same Water Sample	
R27DM	291	45.87	Same Water Sample	Methanol Injection. Pipe in vertical position.
R28DEG	291	45	600 ml De-ionized water	Ethylene glycol injection. Run was aborted due to injection pump problem.
R28DEG	1000	44	Same Water Sample	Repeat previous run. 221 ml of Ethylene glycol was injected. Pipe in vertical position.
R29DNL	1017	46.56	500 ml De-ionized water	20 wt% NaCl inj. Pipe vertical, 750 ml of solution was recovered.
R30DM	1017	44	500 ml De-ionized water	Methanol injection. Pipe in vertical position. 886 ml of solution was recovered after this run.

Table 2- Hydrate plug decomposition runs used for model verification.

Run ID	Decomposition		
	Press. (psia)	Temp. (°F)	$\Delta p$ (psia)
R15D	211	45.25	57.6
R16D	211	45.25	57.6
R17D	211	45.40	60.1
R20D	211	50.48	160.1
R23D	150	51.30	240.5

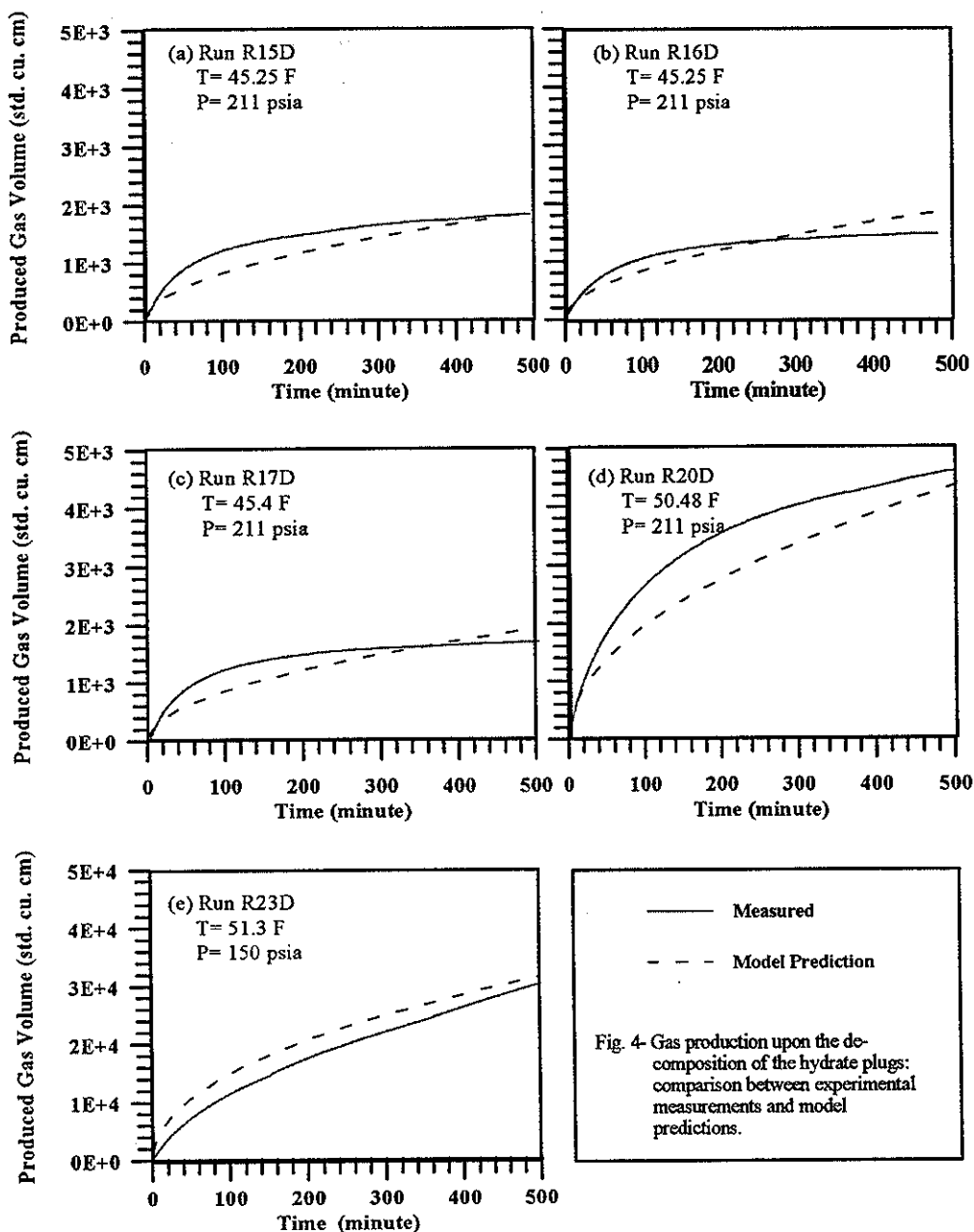
Table 3- Physical parameters of the hydrate plugs.

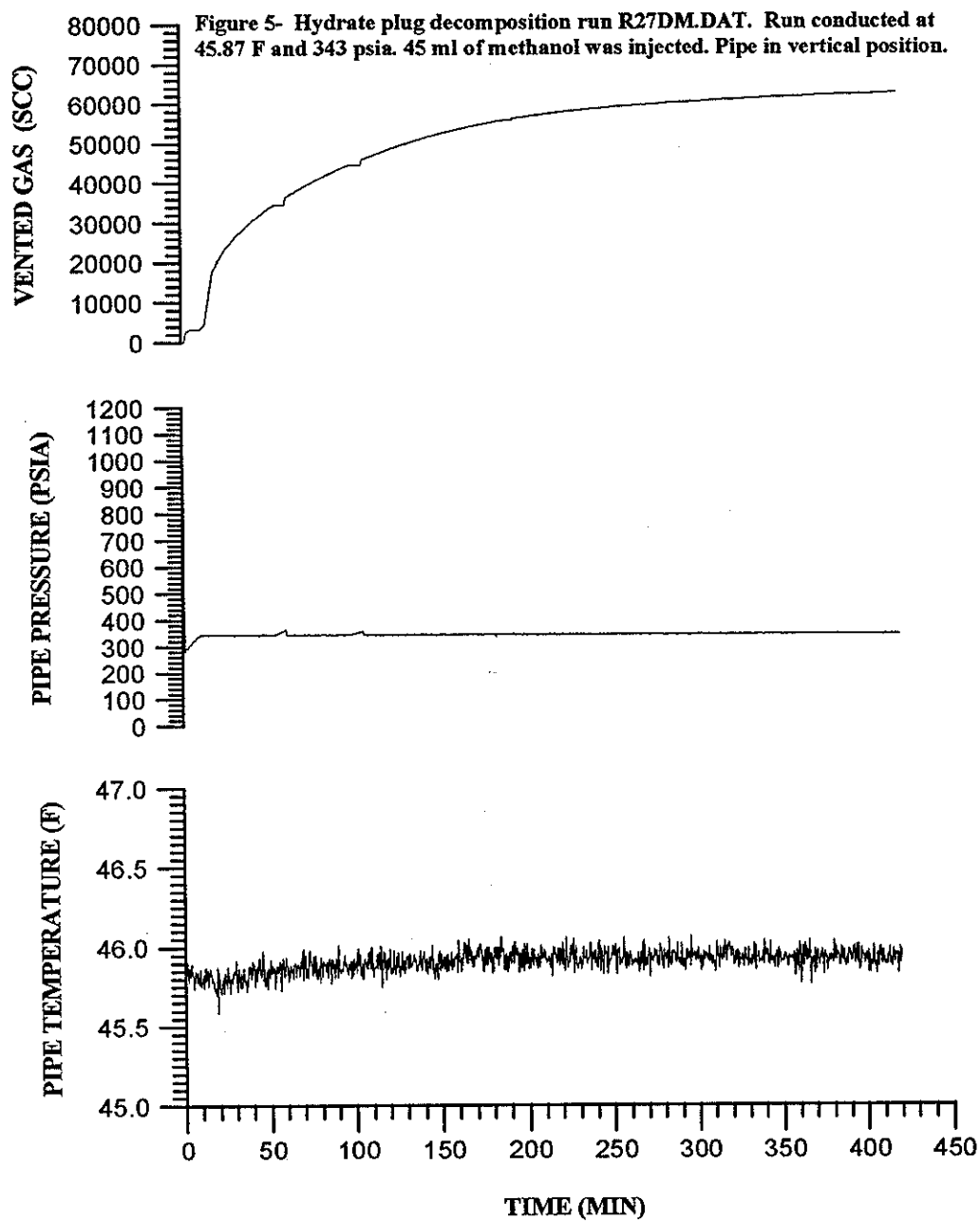
L, plug length	0.33 m
R, plug radius	0.0508 m
c, hydrate heat capacity	275.12e+3 W.s/kmol.K
k, hydrate thermal conductivity	0.45 W/m.K
$\rho$ , density of hydrate	50.8 kmol/m <sup>3</sup>
$\Delta H_d$ , enthalpy of hydrate dissociation	57.7e+6 W.s/kmol

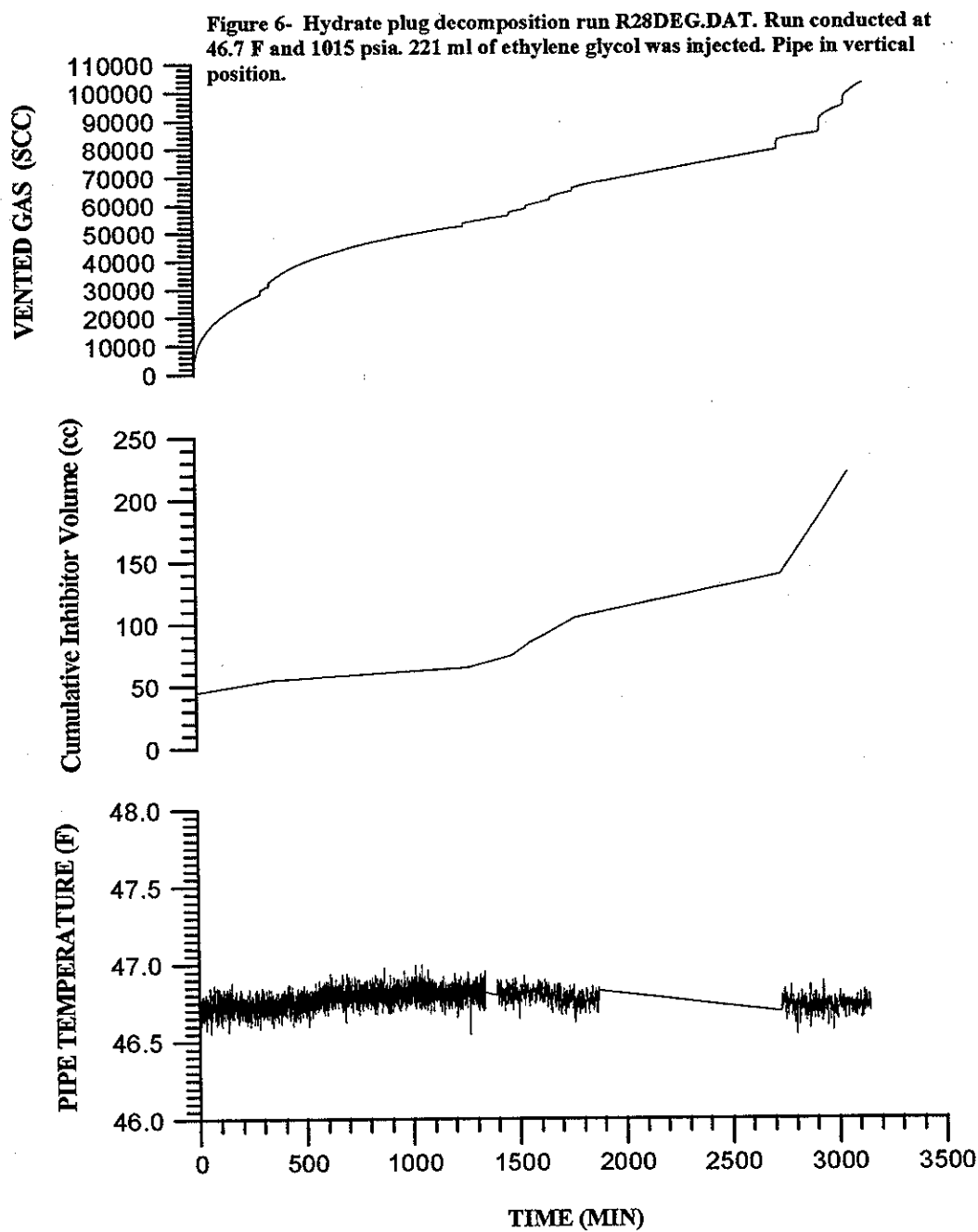
The model predictions of the gas volume resulting from the decomposition of the hydrate plugs is shown in **Fig. 4** as dotted lines. Despite the fact that the model contains no adjustable parameters, it reasonably fits the measured gas production. **Table 3** contains the physical parameters of the hydrates used in the model prediction.

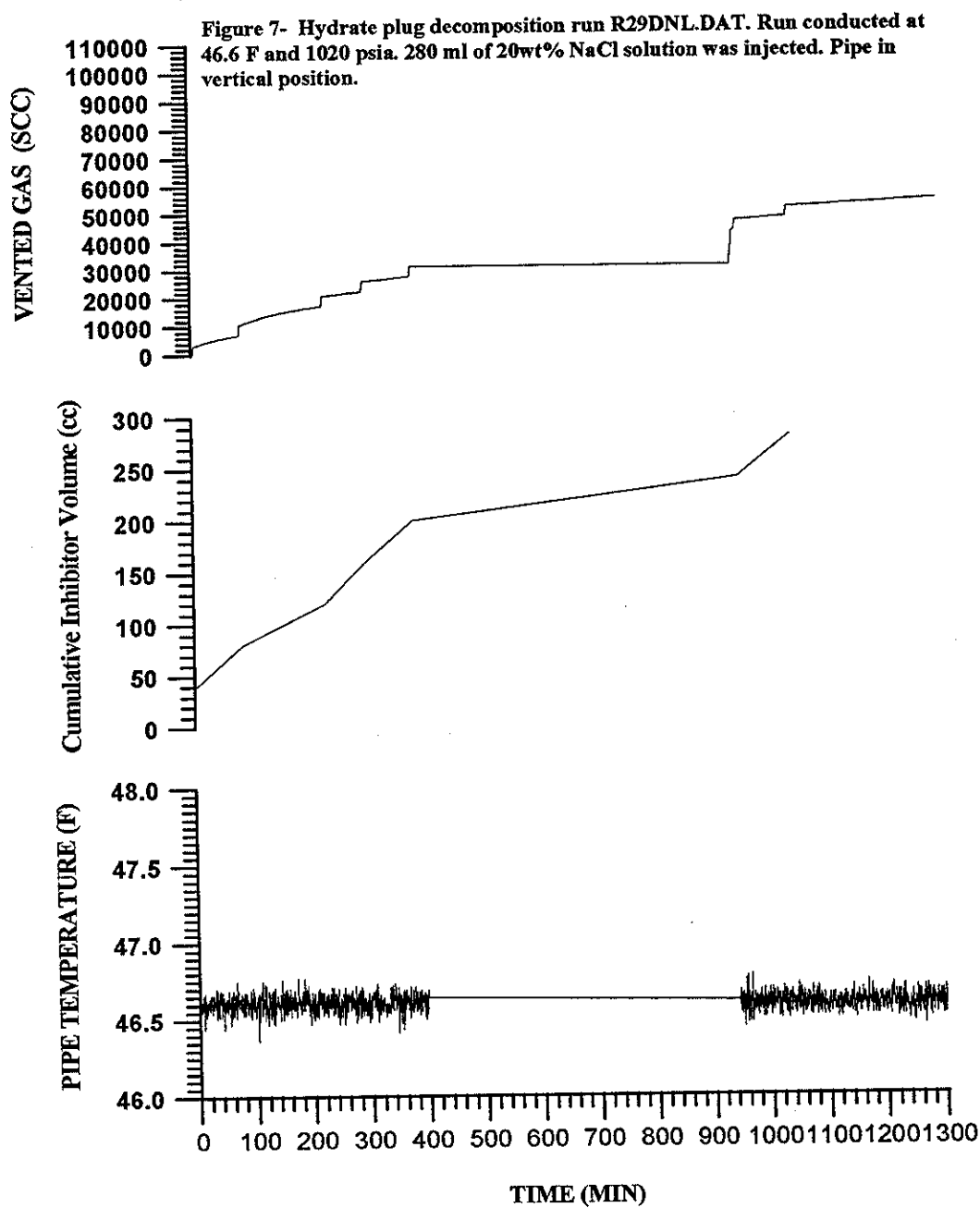
The Data for hydrate plug decomposition by chemical injection are presented in **Figs. 5** through **8**. The tests were done using methanol, ethylene glycol, and NaCl solutions. **Fig. 5** shows the hydrate plug decomposition by methanol injection at 45.87°F and 343 psia. The decomposition was very fast because of the low venting pressure used in this run. In **Fig. 8**, methanol was injected at 46.7°F and 1017 psia. The injection was done in increments of 40-45 ml of methanol. The melting process stopped shortly after the injection of each volume increment of methanol. The plug didn't completely melt until 424 ml was injected.

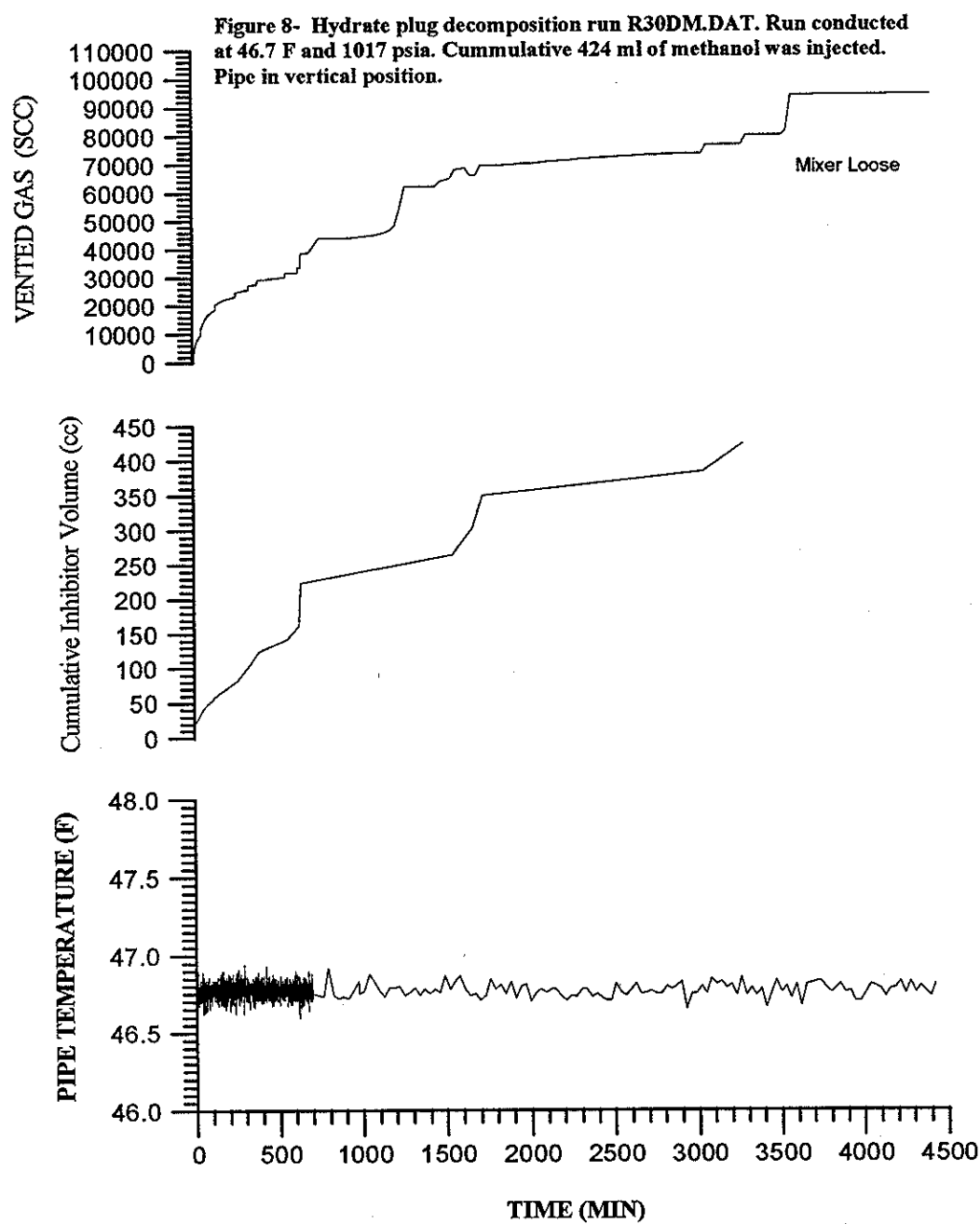
Figure 4 - Gas production upon the decomposition of the hydrate plugs: comparison between experimental measurements and model predictions.













In the test of ethylene glycol injection at 46.7°F and 1015 psia, melting continued for a long time after each injected increment. **Fig. 6** shows the test results. In conclusion, ethylene glycol is a better chemical to use to melt a hydrate plug, especially in vertical pipe sections.

**Fig. 7** shows the test results of 20 wt% NaCl solution at 46.6°F and 1020 psia. The melting rate was similar to the methanol injection test, but considerably slower than the ethylene glycol injection test.

## 5.0 Conclusions

1. Hydrate plugs were formed in a laboratory device specifically designed to examine hydrate formation and decomposition under pipeline operating conditions.
2. Hydrate blockage removal using depressurization is a slow process when conducted at low temperature and small pressure reduction.
3. The plug decomposition process follows different modes depending on the ambient temperature and the magnitude of the pressure reduction.
4. A moving boundary mathematical model developed herein matches the experimental data.
5. In comparison to methanol and salt solutions, ethylene glycol is a better chemical to use to melt a hydrate plug, especially in vertical pipe sections.

## 6.0 Nomenclature

- A: Plug cross-sectional area  
c: Hydrate heat capacity  
h: Heat transfer coefficient  
k: Thermal conductivity  
T: Plug temperature  
T<sub>e</sub>: Sea bed temperature  
t: Time  
ρ: Density of hydrate  
λ: Root of Equations 5 and 11  
ΔH<sub>d</sub>: Enthalpy of hydrate dissociation  
p<sub>e</sub>: Hydrate equilibrium pressure  
p<sub>v</sub>: Pipeline venting pressure  
T<sub>v</sub>: Equilibrium temperature at the venting pressure  
Z(t): Location of plug/gas interface  
V: Gas volume per unit length of the hydrate plug  
R<sub>0</sub>: Initial hydrate plug radius  
G: Volume of gas generated from the decomposition of a unit volume of hydrate  
L: Hydrate plug length